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Thermochimica Acta 389 (2002) 167–177

thermochimica
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An analytical pressure–temperature–composition correlation for the VLE of CO_2 binary mixtures

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Received 26 July 2001; received in revised form 2 November 2001; accepted 21 January 2002

Abstract

An analytical expression relating the vapour–liquid equilibrium pressure, temperature and composition of binary mixtures formed by CO_2 and a non-polar fluid is proposed. The model is based on a simple analytical expression for the vapour pressure of pure non-polar fluids which, for a given temperature, only requires as input the Lennard-Jones molecular parameters and the acentric factor values. A properly modified Lorentz–Berthelot mixing rule is used, the interaction parameters being given as simple functions of temperature and composition with eight constants for each binary mixture. The model is shown to reproduce accurately and in a simple way the pressure (for a given liquid mole fraction) or the liquid composition (for a given pressure) of nine CO_2 + hydrocarbon systems at different temperatures. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Binary mixtures; Vapour–liquid equilibrium

1. Introduction

The design and simulation of chemical processes such as those involving carbon dioxide requires the use of reliable models that generate phase equilibrium properties. Equations of state (EOSs) are generally considered the most appropriate models to calculate the phase equilibrium of mixtures, one of their clear advantages being that, at least theoretically, any thermodynamic property can be obtained and related to any other. Another advantage is that the required procedures have been widely studied and are well known. Nevertheless, when the properties of interest are those of phase equilibrium and, in particular, of vapour–liquid equilibrium (VLE), the method, although accurate in a great number of cases, is not simple or straightforward. We shall briefly discuss the reasons for these difficulties.

First, as Ashour and Aly have indicated [1], no single EOS currently exists that is equally suitable for the prediction of VLE of all classes of binary systems, and over the whole range of temperature, pressure and molecular variety. There are thousands of EOSs that can be selected [1–5] and new proposals are being published every day. Two EOSs which only differ in the temperature dependence of the attractive term may lead to widely different predictions [5]. Moreover, using different sources for the numerical values of the input parameters may also affect the results [5]. Despite the number of reviews on the subject [6–8] there as yet seems to be no clear idea of which equations should be used to obtain the best result for each mixture and for each pressure range.

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PII: S0040-6031(02)00016-3

Second, the application of an EOS to mixtures requires the use of mixing rules to calculate the EOS parameters. The most common method to establish these rules is to assume that the cross-interaction between molecules of different components has the same analytical form as the potential function for pure substances, for example, the Lennard-Jones (LJ) potential. Thus, the most frequently used combining rules for the LJ parameters σ and ε are given by [9]

$$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22}) \quad \text{(Lorentz rule)} \tag{1}$$

and

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2} \quad \text{(Berthelot rule)} \tag{2}$$

where σ_{11} and ε_{11} are the LJ parameters of component 1 and σ_{22} and ε_{22} those of component 2. As is well known, the parameter σ is the distance at which the potential is zero, giving thus an indication of the size of the molecule, and the parameter ε is the absolute value of the depth of the potential well, representing the intensity of the attractive intermolecular forces.

To improve the efficacy of rules given by Eqs. (1) and (2), binary interaction parameters are usually added. Values for these parameters are obtained by a regression analysis of experimental data for the binary mixture. Several authors [10–12] have proposed density- or composition-dependent mixing rules to improve the description of the phase behaviour of strongly non-ideal fluid mixtures. These new mixing rules have been quite successful but their application is not simple. A further study is needed [13] to establish which mixing rule should be used for a particular mixture.

Third, computational methods must be used to solve the equations resulting from equating the fugacities of both components in the two phases. Nevertheless, the use of a particular method is not straightforward and the use of a different method may affect the final result [8,14].

Fourth, the binary interaction parameters are usually obtained by fitting the experimental phase equilibrium data at each temperature. This means that values for the parameters must be calculated at each temperature. For temperatures where no experimental data are available, these values have to be estimated. On the other hand, it is well known that the binary interaction parameters are quite sensitive to many factors including the temperature and pressure range, the composition range and the quality of the experimental data [5]. Although several relationships for the binary interaction parameters have been presented in the literature, they are not always suitable for extrapolation [15]. Moreover, some of these expressions are only suitable for hydrocarbon mixtures [16].

Some of these difficulties can be solved by using an EOS based on molecular parameters [2,17–19]. Although this approach has been shown to lead to accurate results, the analytical forms proposed for the molecular EOS are generally difficult to handle.

We have recently proposed new molecular models for calculating the vapour pressure, the saturation liquid density and the vaporisation enthalpy of pure non-polar fluids [20,21]. In comparison with the methods based on an EOS, the proposed models enable us to calculate directly and straightforwardly these properties only from the LJ parameters (whose values are obtained following the method described by Cuadros et al. [22]), and the acentric factor of a given substance. The aim of the present work is to show how VLE data for binary mixtures of CO_2 with non-polar fluids can be obtained from the vapour pressure model for the pure fluids.

2. Molecular model for pure non-polar fluids

As a first approximation, we shall consider that the molecules of non-polar fluids interact according to the LJ potential [9,23] with adequate values [22] for the molecular parameters ε and σ. Using these parameters, any physical property is then expressed in a dimensional units. The pressure, P (Pa), the density, ρ (mol m^{-3}), and the temperature, T (K), in real units are related to the reduced quantities P^*, ρ^* and T^* by the following relations:

$$P = P^* \frac{(\varepsilon/k)R}{N_a\sigma^3}, \qquad \rho = \frac{\rho^*}{N_a\sigma^3}, \qquad T = T^*(\varepsilon/k) \tag{3}$$

where k is Boltzmann's constant, N_a Avogadro's number, and R is the ideal gas constant. The parameters ε/k and σ are expressed in kelvin and meters, respectively.

In previous papers [20,24] we have shown as the VLE properties of the LJ fluid can be expressed, in good approximation, as a polynomial in the temperature.

Thus, the following expression was obtained for the vapour pressure:

$$P_\mathrm{v}^{*\mathrm{LJ}}(T^*) = -0.530964 + 2.422916T^* - 4.074344T^{*2} + 2.934668T^{*3} - 0.724252T^{*4} \qquad (4)$$

We have also show that for a great number of non-polar fluid, the vapour pressure at a given temperature, $P_\mathrm{v}^*(\omega, T^*)$, can be obtained from

$$P_\mathrm{v}^*(\omega, T^*) = P_\mathrm{v}^{*\mathrm{LJ}}(T^*) + f(\omega, T^*) \qquad (5)$$

where $P_\mathrm{v}^{*\mathrm{LJ}}(T)$ is given by Eq. (4), and $f(\omega, T^*)$ is an universal (in reduced units) function given by

$$f(\omega, T^*) = \sum_{i=0}^{4} a_i T^{*i} + \omega \sum_{i=5}^{9} a_i T^{*i-5} + \omega^2 \sum_{i=10}^{13} a_i T^{*i-10} \qquad (6)$$

where ω is the acentric factor [25]. The universal coefficients a_i have been obtained [20] from a fit to vapour pressure data [26] for 47 substances and are listed in Table 1.

The procedure described above was also used to obtain the density of the liquid phase and the latent heat of vaporisation of these non-polar fluids [21]. In all cases, the models start out from the corresponding property of the LJ reference system, which is perturbed appropriately.

Table 2 lists the molecular parameter values used for the non-polar fluids chosen for this work. The second and third columns give the LJ parameters [22] and the fourth column gives the corresponding values of the acentric factor. The fifth column gives the temperature interval covered for each substance in the fit to the experimental vapour pressure, and the sixth column gives the mean absolute deviation ΔP_v between the experimental values of the vapour pressure [26] and those obtained from Eq. (5).

Table 1
Coefficients of Eq. (6) obtained by correlation of experimental vapour pressure data [26] for 47 pure non-polar fluids

a_0	0.551490
a_1	−2.484688
a_2	4.200572
a_3	−3.156220
a_4	0.883756
a_5	−1.585263
a_6	5.602518
a_7	−6.725159
a_8	3.043007
a_9	−0.417099
a_{10}	0.028668
a_{11}	−1.346791
a_{12}	2.699790
a_{13}	−1.302182

3. Molecular model for binary mixtures

The model for the vapour pressure of pure fluids presented in the previous section, will be now used to model properties related to VLE of binary mixtures of non-polar fluids. To this end, we shall assume that the vapour pressure of a given mixture obeys the law:

$$P_\mathrm{m}(T, x_1) = x_1 P_1(\omega_1, T) + x_2 P_2(\omega_2, T) + x_1 x_2 P_{12}(\omega_{12}, T) \qquad (7)$$

Table 2
Pure component properties used in the present study, temperature range covered, and percent mean absolute deviation ΔP_v between experimental vapour pressure values [26] and those obtained from Eq. (5)

Substance	ε/k (K)	σ (nm)	ω	Temperature range (K)	ΔP_v (%)
Carbon dioxide	201.71	0.4444	0.2310	216.8–262.2	0.17
Methane	140.42	0.4015	0.0130	105.5–182.9	0.71
Propane	255.18	0.5471	0.1530	204.1–331.7	1.99
Cyclopentane	346.11	0.6100	0.1960	285.5–449.9	2.27
n-Butane	287.20	0.6081	0.2010	236.9–373.4	2.07
Benzene	377.46	0.6174	0.2090	311.4–490.7	2.78
n-Pentane	309.75	0.6709	0.2510	263.3–402.7	2.31
n-Hexane	327.47	0.7319	0.2940	286.5–425.7	4.29
Naphthalene	482.26	0.7557	0.2990	422.0–626.9	3.44
n-Octane	351.42	0.8498	0.3980	316.3–456.9	4.98

where $P_1(\omega_1, T)$ and $P_2(\omega_2, T)$ are the vapour pressures of the pure components, $P_{12}(\omega_{12}, T)$ the contribution to the mixture vapour pressure due to the cross-interactions between unlike molecules, and x_1 and x_2 are the mole fractions of the two components in the liquid phase. The analytical expression of Eq. (7), where all the quantities are expressed in real units, allows to obtain the vapour pressure of both pure fluids when $x_1 = 1$ or $x_2 = 1$. The three functions $P_1(\omega_1, T)$, $P_2(\omega_2, T)$, and $P_{12}(\omega_{12}, T)$, are calculated using Eq. (5), i.e. using the same analytical expression proposed for the vapour pressure of pure fluids. Since Eq. (5) is given in terms of reduced units, one has to use the molecular parameters of the first component (ε_1, σ_1, ω_1) to obtain the real values of $P_1(\omega_1, T)$ and those of the second component (ε_2, σ_2, ω_2), to obtain real values of $P_2(\omega_2, T)$. Values for $P_{12}(\omega_{12}, T)$ will be obtained using mixing rules for ε_{12}, σ_{12} and ω_{12} in terms of the molecular parameters of the pure components. Taking into account that, as was indicated in the Introduction, the binary interaction parameters are quite sensitive to many factors, including the temperature, pressure and composition range, we propose the following empirical mixing rules:

$$\varepsilon_{12} = (\varepsilon_1\varepsilon_2)^{1/2}\frac{T}{\tau_1 + \tau_2 T + \tau_3 T^2 + \tau_4 x_1} \tag{8}$$

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}\tau_5 + \tau_6 T + \tau_7 T^2 + \tau_8 x_1 \tag{9}$$

and

$$\omega_{12} = \omega_1 + \omega_2 \tag{10}$$

where τ_i are parameters which adopt different values for each particular mixture, but are independent of temperature, pressure or composition.

In sum, to obtain the vapour pressure of a given mixture for a given temperature and liquid mole fraction, one only needs as input the parameters ε/k, σ, and ω for both pure fluids, and the τ_i coefficients for this mixture. Moreover, the liquid mole fraction x_1 may be obtained by solving Eq. (7) for a given temperature and pressure.

In the following section, we shall discuss the results obtained when this model is used to reproduce the vapour pressure and mole fraction of binary mixtures of CO_2 with nine non-polar fluids.

4. Results

Table 3 lists the values for the empirical coefficients τ_i ($i = 1, 2, \ldots, 8$) of Eqs. (8) and (9) for the nine systems studied. These values were obtained by comparing the vapour pressure values obtained from Eq. (7) and the experimental data for each system described in Table 4. A theoretical interpretation of these parameters can not be easily given from the obtained values. In any case, a more detailed theoretical study and the consideration of different binary systems could lead, at least, to a correlation of those parameters with some of the microscopic properties of the systems.

Table 4 gives a description of VLE data used in this study and the results obtained for P_m and x_1 using Eq. (7). The first column lists the system and the second column indicates the number of data points used in the fit. The third and fourth columns list the temperature and the pressure range, respectively. The fifth column lists the experimental mole fraction range for the first component (i.e. for CO_2, except for the methane + CO_2 and octane + CO_2 systems). The sixth and seventh columns give the absolute relative deviation between experimental and calculated vapour pressure, ΔP_m, and between experimental and calculated mole fractions, Δx_1, for each isothermal set of data, and the mean deviations for each of the systems studied (bold numbers). The last column gives the source of data [27–41].

As may be seen in Table 4, the proposed molecular model, Eq. (7), reproduces the vapour pressures of these binary mixtures with mean absolute deviations lower than 8.5% for a given temperature. For each system, mean absolute deviations ranging from 0.4 to 4.3% are found.

Fig. 1 shows the percent deviations (%) between experimental [34] and calculated vapour pressures for each data point of the CO_2 + cyclopentane system. Although this system presents the highest mean deviation (see Table 4), Fig. 1 shows that the model gives a reasonable estimate of the experimental data, since the individual deviations are less than 6.5% for most of points, with a few exceptions at lowest pressures.

With respect to the mole fraction x_1, this quantity is predicted with mean deviations lower than 8.1% for each isothermal set of data studied. The only

Table 3
Values for the τ_i coefficients of Eqs. (8) and (9) for the CO_2 + hydrocarbon systems studied in this paper

τ_i	Methane + CO_2	CO_2 + propane	CO_2 + cyclopentane	CO_2 + *n*-butane	CO_2 + benzene	CO_2 + *n*-pentane	CO_2 + *n*-hexane	CO_2 + naphthalene	Octane + CO_2
τ_1 (K)	5.52096×10^{11}	-4.26022×10^{10}	6.56528×10^{10}	1.19365×10^{12}	2.7281×10^{12}	6.46683×10^{10}	-6.96526×10^{10}	2.84585×10^{11}	-1.84209×10^{11}
τ_2	-6.56982×10^{9}	1.4626×10^{9}	-3.4592×10^{8}	-6.01087×10^{9}	-1.09439×10^{10}	2.93758×10^{8}	5.36857×10^{8}	-1.10749×10^{9}	1.19771×10^{9}
τ_3 (K^{-1})	1.69062×10^{7}	-4.01259×10^{6}	483115.0	6.93922×10^{6}	9.06454×10^{6}	-1.62499×10^{6}	−993908.0	723398.0	-1.94785×10^{6}
τ_4 (K)	1.17857×10^{11}	-2.78086×10^{10}	-7.62388×10^{9}	-3.40784×10^{10}	-8.8206×10^{10}	2.08347×10^{10}	-2.44493×10^{9}	-9.3143×10^{9}	1.37622×10^{9}
τ_5	-3.958558×10^{9}	-9.16432×10^{8}	3.91625×10^{8}	1.49909×10^{9}	-9.99734×10^{9}	2.97592×10^{8}	-2.24447×10^{8}	6.25118×10^{8}	-2.1302×10^{8}
τ_6 (K^{-1})	3.066316×10^{7}	5.39788×10^{6}	-2.53626×10^{6}	-9.0129×10^{6}	5.4266×10^{7}	-1.73241×10^{6}	1.46026×10^{6}	−107273.0	1.44651×10^{6}
τ_7 (K^{-2})	−62577.92	−8170.96	4019.0	12203.4	−75353.7	1629.52	−2435.62	−3784.76	−2442.02
τ_8	2.546378×10^{8}	2.52687×10^{7}	6.18075×10^{6}	5.20862×10^{7}	4.36649×10^{7}	4.27593×10^{7}	3.4309×10^{6}	-1.82152×10^{7}	-4.61848×10^{6}

Each set of τ_i values is obtained by comparison of experimental VLE data and values calculated using Eq. (7).

Table 4
Correlation of VLE data for the CO_2 + hydrocarbon systems using Eq. (7): number of data points for each system, conditions and source of experimental data, the percent absolute deviation between experimental and calculated vapour pressure, ΔP_m, and between experimental and calculated mole fractions, Δx_1, for each isothermal set of data, and the mean deviations for each of the systems studied (bold numbers)

Binary mixture	Data number	Temperature (K)	P range (MPa)	x_1 range	ΔP_m (%)	Δx_1 (%)	Reference
Methane + CO_2	84	153.15	1.16–1.17	0.9919–0.9973	1.5	1.0	[27]
		173.15	2.46–2.55	0.9507–0.9809	0.1	0.1	
		183.15	3.36–3.58	0.9350–0.9872	0.4	0.4	
		193.15	4.29–4.74	0.8853–0.9736	0.7	0.9	
		203.15	4.83–5.34	0.7307–0.8784	3.1	5.0	
		210.15	4.22–5.83	0.3062–0.8370	5.8	15.6	
		219.26	0.69–6.47	0.0049–0.7483	1.9	3.4	
		230	1.52–7.14	0.027–0.584	3.7	5.2	[28]
		250	2.03–8.09	0.010–0.446	6.1	13.4	
		270	3.55–8.52	0.014–0.319	2.4	6.9	
					3.1	**6.4**	
CO_2 + propane	166	233.15	0.35–0.69	0.165–0.528	5.1	8.0	[29]
		244.26	0.50–1.36	0.1134–0.8067	8.4	16.6	[30]
		252.95	0.33–1.83	0.030–0.868	3.4	7.3	[31]
		266.48	0.81–2.61	0.0886–0.8189	3.0	5.5	[30]
		273.15	0.56–3.43	0.013–0.953	5.0	14.4	[31]
		294.26	1.03–5.86	0.0245–0.9805	5.6	9.5	[32]
		310.93	1.38–6.89	0.0081–0.7902	2.4	6.7	
		311.05	1.49–6.70	0.0199–0.7800	1.2	3.0	[33]
		327.75	2.19–6.46	0.0293–0.5594	2.2	4.5	
		344.43	2.89–5.98	0.0214–0.3643	1.9	5.4	
		361.15	3.80–4.96	0.0125–0.1444	1.0	7.1	
					2.8	**6.4**	
CO_2 + cyclopentane	39	310.86	0.18–6.55	0.0067–0.857	5.4	7.8	[34]
		318.17	0.65–7.36	0.048–0.844	4.3	6.2	
		333.17	1.07–8.26	0.058–0.726	3.1	3.9	
					4.3	**6.0**	
CO_2 + *n*-butane	106	311.09	0.59–7.52	0.0245–0.9388	2.6	3.8	[35]
		344.43	0.99–8.06	0.0108–0.7000	1.6	2.6	
		394.60	2.48–6.51	0.0110–0.3535	1.1	3.6	
					1.9	**3.3**	
CO_2 + benzene	29	313.4	2.12–5.92	0.190–0.661	1.3	1.5	[36]
		353.0	0.49–6.27	0.020–0.332	3.4	4.2	
		373.5	0.67–5.91	0.023–0.280	1.5	1.7	
		393.2	0.73–5.95	0.017–0.249	1.5	2.0	
					1.9	**2.4**	
CO_2 + *n*-pentane	48	277.65	0.23–3.90	0.0290–0.9791	1.4	1.7	[37]
		311.04	0.46–7.38	0.0344–0.9416	4.0	5.4	
		344.15	0.41–9.22	0.0072–0.7796	3.8	5.7	
		377.59	0.91–9.63	0.0119–0.6447	3.7	6.3	
					3.4	**4.9**	
CO_2 + *n*-hexane	50	273.15	1.07–3.15	0.188–0.9019	4.7	7.8	[38]
		283.15	1.24–4.01	0.188–0.9019	4.9	6.0	
		298.15	1.53–5.54	0.188–0.9019	3.9	5.0	
		303.15	1.62–6.75	0.188–0.966	4.7	5.5	[38,39]
		313.15	2.08–7.87	0.217–0.952	2.0	2.2	[39]
		323.15	1.86–8.49	0.175–0.919	1.3	1.5	
					3.5	**4.4**	

Table 4 (*Continued*)

Binary mixture	Data number	Temperature (K)	P range (MPa)	x_1 range	ΔP_m (%)	Δx_1 (%)	Reference
CO_2 + naphthalene	14	373.2	1.39–10.45	0.047–0.336	0.5	0.5	[40]
		423.2	1.93–9.97	0.051–0.252	0.3	0.3	
					0.4	**0.4**	
Octane + CO_2	20	313.15	1.50–7.55	0.8567–0.1100	0.8	1.0	[41]
		328.15	2.00–9.50	0.8260–0.1185	1.8	1.4	
		348.15	2.00–11.35	0.8550–0.1870	3.2	3.1	
					2.0	**2.0**	

exceptions are the higher deviations obtained at four temperatures for the methane + CO_2 and CO_2 + propane mixtures (Table 4). This is a reasonable results, because high deviations have been also found in the calculation of the pressure at these four temperatures. Values for the mean deviations for each system range from 0.4 to 6.4%.

We have compared some of the results presented in this paper with those previously obtained by others authors by using EOS. In particular, Table 5 shows a comparison for three systems (CO_2 + benzene, CO_2 + naphthalene and CO_2 + pentane) at the same temperature, pressure and mole fraction ranges used in our fits. It may be observed that the deviations between experimental values for the CO_2 + benzene and CO_2 + naphthalene equilibrium pressure and values obtained using our model are lower than those obtained by Yau and Tsai [7] using the Soave EOS. For the CO_2 + pentane mixture, the accuracy of our results is similar to the obtained by Anderko [3] by using their own EOS and a correlation for the binary interaction parameter.

Results obtained by using Eq. (7) for some other mixtures are also as accurate as those obtained through

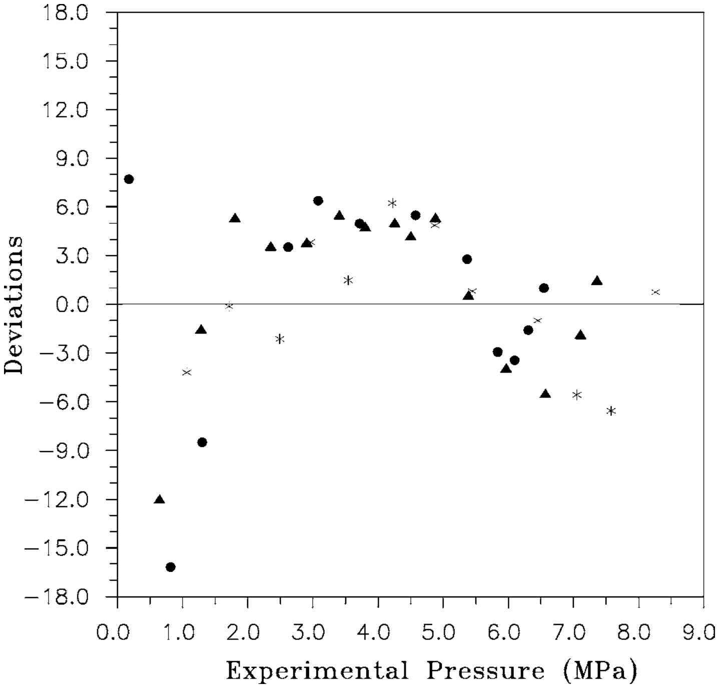

Fig. 1. The individual percent deviations between the experimental [34] vapour pressure data for the CO_2 + cyclopentane system and those calculated using Eq. (7): (●) 310.86 K; (▲) 318.17 K; (*) 333.17 K.

Table 5
Comparison between vapour pressures obtained using the model proposed in this paper, Eq. (7), and those obtained by others authors using an EOS

Binary mixture	Temperature (K)	ΔP (%)	ΔP (%) this work
CO_2 + benzene [36]	313.4	2.9[a]	1.3
	353.0	4.1[a]	3.4
	373.5	2.2[a]	1.5
	393.2	3.3[a]	1.5
CO_2 + napthalene [40]	373.2	4.6[a]	0.5
	423.2	2.4[a]	0.3
CO_2 + pentane [37]	277.65	1.3[b]	1.4
	311.04	3.8[b]	4.0
	344.15	3.6[b]	3.8
	377.59	2.9[b]	3.7

[a] From Yau and Tsai [7].
[b] From Anderko [3].

traditional methods. For example, Keshtkar et al. [13] have used the Soave–Redlich–Kwong EOS for the CO_2 + propane to obtain the equilibrium pressure in the temperature range 244–361 K. When these pressure values are compared with the experimental data of Nagahama et al. [31], Hamam and Lu [30], and Niesen and Rainwater [33], the absolute mean deviations values obtained are 4.2% when an UNIFAC-based Huron–Vidal modified mixing rule is used, and 2.7% when a second more complex modification is used. In comparison, a mean absolute deviation of 2.8% is obtained for a similar temperature range (233–361 K) when our model is used.

We have also compared results for the pressure of the methane + CO_2 mixtures at temperatures ranging from 153 to 271 K. For that temperature range, Keshtkar et al. have obtained [13] mean absolute deviations of 2.4 and 1.8% using the above-mentioned modifications of the Huron–Vidal mixture rules, whereas a deviation of 3.1% is obtained by means of Eq. (7).

As an example of the results obtained, Fig. 2 shows plots of pressure versus composition for the CO_2 + pentane system. The experimental data [37] are plotted together with vapour pressure values calculated at four temperatures using Eq. (7). It may be observed that there is good agreement between our

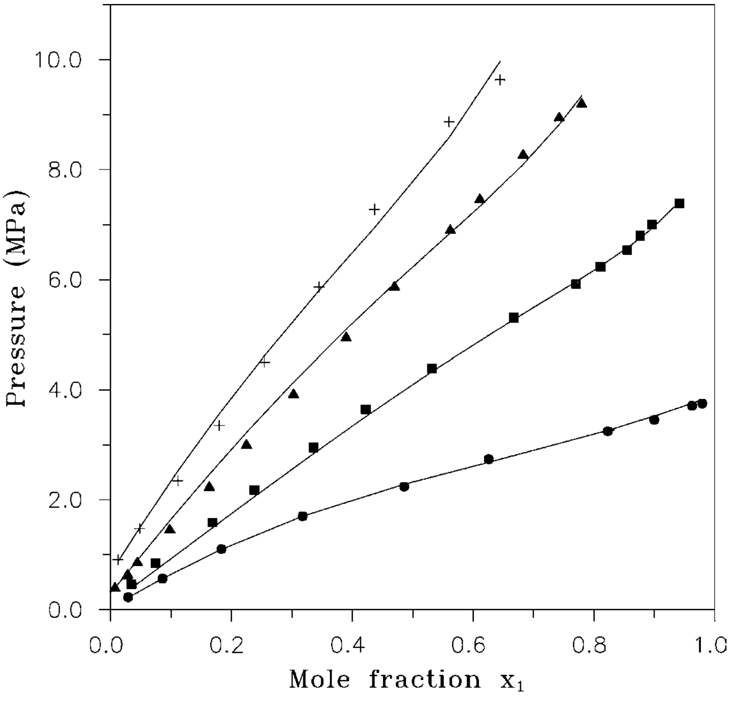

Fig. 2. VLE data for the CO_2 + pentane system [37]: (●) 277.65 K; (■) 311.04 K; (▲) 344.15 K; (+) 377.59 K; (—) calculated values for the vapour pressure obtained from the model proposed in this paper (Eq. (7)).

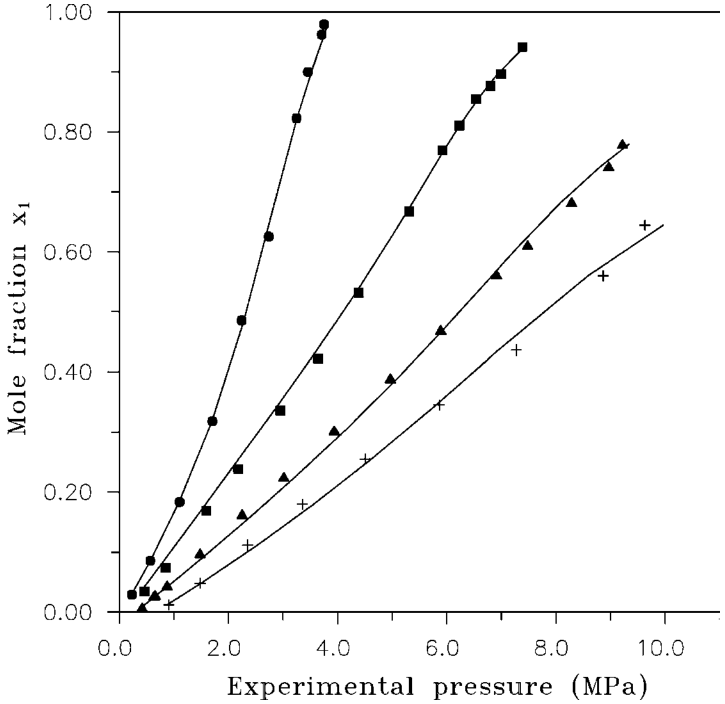

Fig. 3. VLE data for the CO_2 + pentane system [37]: (●) 277.65 K; (■) 311.04 K; (▲) 344.15 K; (+) 377.59 K; (—) calculated values for the liquid composition obtained from the model proposed in this paper (Eq. (7)).

results and the experimental data. Deviations for each data point are lower than 7%, except for a few points at the lowest mole fraction values.

Fig. 3 shows plots of composition versus pressure for the CO_2 + pentane system. The experimental data [37] are plotted together with composition values calculated at four temperatures using Eq. (7). Again, the agreement between our results and the experimental data is very good and the individual deviations are lower than 8%, except for some points at the lowest pressures.

Therefore, the model proposed here allows to predict the vapour pressure of the mixture for any temperature and mole fraction within the ranges considered, and also allows the mole fraction to be predicted for any given temperature and pressure within those ranges. No specific parameters for each temperature are required, as is usually the case for the binary interaction parameter used in the EOS method, and there are not simultaneous equations to be solved except the trivial calculation of mole fraction for a given temperature and pressure using Eq. (7).

5. Conclusions

An analytical expression relating the pressure, temperature, and composition for the VLE of non-polar binary mixtures is proposed. The model is based on a simple analytical expression for the vapour pressure of pure fluids. The equilibrium pressure for the mixture is then expressed in terms of the vapour pressure of each component and a mixture contribution. The molecular parameters for the mixture contribution are obtained from modified Lorentz–Berthelot mixing rules, where the interaction parameters are given as simple functions of the temperature and composition, with eight adjustable empirical parameters for each system that could be obtained from a small number of reliable experimental data. Since the mixing rules are defined by these constants, their final expressions have the same analytical form for any mixture. A physical interpretation of these parameters can not be given by merely analysing results for CO_2 mixtures.

The appropriate constants for nine different CO_2 + hydrocarbon systems are obtained in this study. It should be noted that these constants can be used for any temperature, composition or pressure within or near the studied ranges of temperature and pressure, for the selected systems. We have shown that the model is able to reproduce the pressure (for a given liquid mole fraction) or the liquid composition (for a given pressure) in a simple way. For the pressure, mean deviations with respect to experimental data range from 0.4 to 4.3% for each system, being less than 8.5% for a given isothermal data set. The liquid mole fraction can be obtained with mean deviations ranging from 0.4 to 6.4% for each mixture, being less than 8.1% for most of the isothermal data sets.

The proposed model does not require to solve systems of equations, contrary to the case of the EOS. Pressures, may be calculated easily and straightforwardly through simple polynomial expressions. If the liquid mole fraction is required a simple polynomial equation must be solved.

We are now applying the method to other mixtures, in order to find a possible physical interpretation of the proposed mixture rules. The presented approach may be extended in the future to include the calculation of VLE for multicomponent systems. Another possibility would be the simultaneous correlation of VLE data and other thermodynamic properties in the critical and supercritical regions.

Acknowledgements

The authors express their gratitude to the Consejería de Educación y Juventud of the Junta de Extremadura and to the Fondo Social Europeo for the financial aid granted through the Project IPR98B004. C.A. Faúndez would like to express his gratitude to the Agencia Española de Cooperación Internacional (AECI) for its support through a MUTIS grant, as well as to the Departamento de Física de la Universidad de Extremadura (Spain) for facilitating his stay.

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